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(54) DEPROTEINIZATION TREATING AGENT AND PRODUCTION OF CATIONIC DEPROTEINIZED NATURAL RUBBER LATEX USING THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a deproteinization treating agent for obtaining a stable natural rubber latex exhibiting cationic properties and having high safety and to provide a method for producing a cationic deproteinized natural rubber latex using the deproteinization treating agent.
SOLUTION: This deproteinization treating agent comprises a proteolytic enzyme such as an alkaline protease and one or more cationic surfactants selected from the group consisting of alkylamine salts, alkylamine derivatives and quaternized substances thereof. The cationic deproteinized natural rubber latex is produced by adding the deproteinization treating agent to a field latex or an ammonia-treated latex, carrying out a deproteinization treatment and then purifying rubber particles in the latex.

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* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] The deproteinization agent which consists of a proteolytic enzyme and one or more sorts of cationic surfactants chosen from the group which consists of an alkylamine salt, alkylamine derivatives, and the 4th class ghosts of those.
[Claim 2] The deproteinization agent according to claim 1 said whose proteolytic enzyme is alkaline protease.
[Claim 3] The manufacture approach of the cationic deprotein natural rubber latex characterized by refining the rubber particle in a latex after deproteinizing by adding a deproteinization agent according to claim 1 or 2 to a field latex or an ammoniation latex.
[Claim 4] The manufacture approach of the cationic deprotein natural rubber latex according to claim 3 which adds the addition of said deproteinization agent so that the content of the cationic surfactant in the deproteinization agent concerned may serve as 0.1 - 20 weight section to the rubber solid content 100 weight section in a latex.
[Claim 5] The manufacture approach of the cationic deprotein natural rubber latex according to claim 3 or 4 which adds the addition of said deproteinization agent so that the content of the proteolytic enzyme in the deproteinization agent concerned may serve as 0.0001 - 20 weight section to the rubber solid content 100 weight section in a latex.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the manufacture approach of the deproteinization agent for obtaining the deprotein [in which it is stable and cationicity is shown] natural rubber latex from which the protein in natural rubber was removed, and the cationic deprotein natural rubber latex using it.
[0002]
[Description of the Prior Art] Generally, although natural rubber latex contains protein as non-rubber components other than a rubber component, since the class and amount of this protein change with places of production, production stages, etc. of a latex, last quality, a last vulcanization property, etc. of a natural rubber product are made to produce dispersion, or electrical properties, such as mechanical characteristics, such as a creep property and aging resistance, and insulation, etc. have become the cause of reducing the quality of a natural rubber product itself.
[0003] When a natural rubber product is furthermore used in recent years, the protein in natural rubber becomes a cause and the case where the allergy symptom of a strong I-beam is caused is reported. Although washing concentration of the natural rubber latex was carried out with water or the approach of adding a surfactant and carrying out washing concentration was indicated to these problems, these approaches of extent of deprotein were insufficient. To these problems, to aim at solution by the approach of removing protein to altitude is tried from the natural rubber latex of the disclosure to JP,6-56904,A, JP,6-56905,A, and JP,6-56906,A. After this approach adds a proteolytic enzyme (protease) and the surfactant of anionic or the Nonion nature to natural rubber latex and disassembles protein, by purification processing by centrifugal separation etc., it separates a cream-like rubber component and removes protein.
[0004] However, the surfactant used by the above-mentioned approach is the thing of anionic or the Nonion nature, and is in the condition of the rubber particle in deprotein natural rubber latex also being charged in negative, or not having a polarity. Therefore, it was unsuitable to have used this latex for raw materials, such as the object-ed charged in negative from the first, for example, fiber, and an adhesive to a paper product.
[0005]
[Problem(s) to be Solved by the Invention] The cationic natural rubber latex which, on the other hand, blended with the 94-95th page of "Natural Rubber Science and Technology" (A.D.Roberts editing, the Oxford university publication, 1988 annual publications) the cetyl trimethylammonium bromide (CTAB) which is a cationic surface active agent is indicated. Although the latex which consists of a rubber particle which has a cation will be obtained like this reference if the cationic surfactant of sufficient amount for natural rubber latex is added, when processed underwater, the adhesion force with fiber, paper leaf, etc. which are charged in negative can be raised by making a latex into cationicity in this way.
[0006] However, only by adding a cationic surfactant, deprotein cannot be attained with a natural thing and safe natural rubber latex cannot be offered to the body -- an allergic response arises. Furthermore, when a cationic surfactant is only added, the problem that a stable latex --

viscosity rises with time and a congelation is generated -- cannot be obtained is in natural rubber latex.
[0007] Then, the object of this invention shows cationicity, and its safety is high, and it is offering the deproteinization agent for obtaining stable natural rubber latex, and the manufacture approach of the cationic deprotein natural rubber latex using it.
[0008]
[The means for solving a technical problem and an effect of the invention] this invention persons came to complete a header and this invention for the completely new data that generating of an allergic response was fully controlled and that a latex with the high safety to the body can also be obtained while being able to get the stable latex which fully controlled generating of a congelation, when deproteinizing by blending a specific cationic surfactant with natural rubber latex, as a result of repeating research wholeheartedly, in order to solve the above-mentioned technical problem.
[0009] That is, the deproteinization agent of this invention is characterized by consisting of a proteolytic enzyme and one or more sorts of cationic surfactants chosen from the group which consists of an alkylamine salt, alkylamine derivatives, and the 4th class ghosts of those. In case the distributed condition of the rubber particle destabilized with deprotein is stabilized with a surfactant like conventional deprotein natural rubber latex according to the deproteinization agent of above-mentioned this invention, a latex is not electrified in negative. Moreover, since the latex to which deproteinization was performed is made to contain a specific cationic surface active agent, generating of a congelation can fully be controlled and a stable latex can be offered. Furthermore, since the protein in natural rubber latex is removed by deproteinization, generating of an allergic response can fully be controlled and natural rubber latex with the high safety to the body can be offered.
[0010] The manufacture approach of the cationic deprotein natural rubber latex of this invention is characterized by adding the deproteinization agent of above-mentioned this invention to a field latex or an ammoniation latex, and refining the rubber particle in a latex. In the manufacture approach of the above-mentioned cationic deprotein natural rubber latex, as for the addition of a deproteinization agent, it is desirable to add so that the content of a surfactant may serve as 0.1 - 20 weight section to the rubber solid content 100 weight section in a latex, and it is desirable to add so that the content of a proteolytic enzyme may serve as 0.0001 - 20 weight section to the rubber solid content 100 weight section in a latex.
[0011]
[Embodiment of the Invention] Hereafter, this invention is explained to a detail.
[Deproteinization agent]
(Proteolytic enzyme) Although a well-known thing is especially usable and is not conventionally limited as a proteolytic enzyme used for the deproteinization agent of this invention, alkaline protease etc. is suitable, for example. As the origin of a protease, although you may be which things, such as a thing of the bacteria origin, a thing of the mold origin, and a thing of the yeast origin, in these, it is the thing of the bacteria origin and especially the thing of a Bacillus group is desirable. Moreover, it is also possible to use together enzymes, such as lipase, esterase, an amylase, a laccase, and a cellulase.
[0012] The protease KAP by Kao Corp. in which especially the proteolytic enzyme used for this invention has the resistance over a surfactant also in the above is used suitably. When using alkaline protease as a proteolytic enzyme, it is preferably suitable for the activity [the measured value by the method of improving the Anson-haemoglobin complex method (22 Anson.M.L., J.Gen.Physiol., 79 (1938))] that it is the range of 1 - 25 APU/g 0.1 to 50 APU/g.
[0013] In case the deproteinization agent of this invention is used for the amount of the above-mentioned proteolytic enzyme used, it is desirable to add so that it may become 0.0001 - 20 weight section to the rubber part 100 weight section in natural rubber latex, and it is more desirable to add in the range of 0.001 - 10 weight section. The effectiveness of fully being able to disassemble the protein in a latex as the amount of the proteolytic enzyme used is said within the limits, and the activity of an enzyme being held, or balancing the amount of the enzyme used can be discovered effectively, and it becomes advantageous in cost.

[0014] It faces manufacturing the cationic deprotein natural rubber latex of this invention. (Surface active agent) (i) It aims at distributing a part for rubber in the stable condition in a latex at the time of decomposition processing of protein. Furthermore should excel the distributed stability and preservation stability of the (ii) latex, and just electrify the rubber particle in a latex, and it aims at considering as the underwater suspension of a cation charged particle. Into a latex, one or more sorts of cationic surfactants as a stabilizer are used.
[0015] As a cationic surfactant used for this invention, an alkylamine salt, alkylamine derivatives, and the 4th class ghosts of those are mentioned. Although the salt of primary amine, secondary amine, and tertiary amine is mentioned and it is not especially limited as the above-mentioned alkylamine salt, as a salt, a hydrochloride, phosphate, acetate, alkyl-sulfuric-acid ester, alkylbenzene sulfonic acid, an alkyl naphthalene sulfonic acid, a fatty acid, an organic acid, alkyl phosphoric ester, an alkyl ether carboxylic acid, an alkylamide ether carboxylic acid, anionic oligomer, an anionic polymer, etc. are mentioned, for example.
[0016] The above-mentioned alkylamine derivative is what has at least one of an ester group, a ether group, and amide groups in intramolecular. For example, polyoxyalkylene (AO) alkylamine and its salt, An alkyl ester amine (AO addition product is included) and its salt, an alkyl ether amine (AO addition product is included), and its salt, An alkylamide amine (AO addition product is included) and its salt, an alkyl ester amide amine (AO addition product is included), and its salt, An alkyl ether amide amine (AO addition product is included), its salt, etc. are mentioned. As a salt For example, a hydrochloride, phosphate, acetate, alkyl-sulfuric-acid ester, alkylbenzene sulfonic acid, An alkyl naphthalene sulfonic acid, a fatty acid, an organic acid, alkyl phosphoric ester, an alkyl ether carboxylic acid, an alkylamide ether carboxylic acid, anionic oligomer, an anionic polymer, etc. are mentioned.
[0017] As an example of the above-mentioned acetate, coconut amine acetate, stearyl amine acetate, etc. are mentioned, for example. Although the above-mentioned alkylamine salt and especially the alkyl group in an alkylamine derivative are not limited, the thing of the shape of the shape of a straight chain, branched-chain, or Guerbet of carbon numbers 8-22 is usually mentioned. as the 4th class ghost of the above-mentioned alkylamine salt and an alkylamine derivative -- the above-mentioned alkylamine salt and an alkylamine derivative -- for example, methyl chloride, a methyl bromide, a dimethyl sulfate, a diethyl sulfate, etc. -- the -- what was formed into 4 class is mentioned.
[0018] As said quarternary ammonium salt, what has the alkyl group of carbon numbers 8-22, for example is mentioned, and dialkyl dimethylannmonium halide; trialkyl methylammonium halide; dialkyl benzyl methylammonium halide; alkyl benzyl dimethylannmonium halide, such as alkyl trimethylammonium halide; distearyldimethylbenzylammonium halide, such as lauryl trimethylammonium halide, cetyl trimethylammonium halide, and stearyl trimethyl ammonium halide, etc. is mentioned in more detail.
[0019] Also in the cationic surface active agent of the above-mentioned instantiation, since the stabilization effect of a latex is excellent, cetyl trimethylammonium chloride (CTAC) and especially stearyl trimethylammonium chloride are used suitable for this invention. In case the deproteinization agent of this invention is used for the amount of the above-mentioned cationic surfactant used, it is desirable to add so that it may become 0.1 - 20 weight section to the rubber solid content 100 weight section in natural rubber latex, and it is more desirable to add in the range of 0.5 - 15 weight section. The hygroscopicity of solid rubber when adsorption of the cationic surface active agent to the rubber particle in a latex dries a next door and a latex enough as the amount of the cationic surface active agent used is said within the limits is maintained low, can discover effectively the effectiveness of balancing the amount used, and becomes advantageous in cost.
[0020] (Other additives) Other additives, such as pH regulator, may be used together on the occasion of using the above-mentioned proteolytic enzyme and a cationic surfactant as a deproteinization agent. As the above-mentioned pH regulator, acetate; sulfates, such as phosphate; potassium acetate, such as a potassium dihydrogenphosphate, potassium phosphate, and disodium hydrogenphosphate, and sodium acetate, a hydrochloride, a nitrate, citrate, succinate, ammonia, a sodium hydroxide, a potassium hydroxide, a sodium carbonate, a sodium

hydrogencarbonate, etc. are mentioned, for example.
[0021] The [manufacture approach of cationic deprotein natural rubber latex] It is suitable to deproteinize by adding the deproteinized-natural-rubber processing agent of this invention to the natural rubber latex which serves as a start raw material in manufacture in the cationic deprotein natural rubber latex using the deproteinized-natural-rubber processing agent of this invention, to perform purification processing of a latex particle subsequently, and to use the approach of removing a proteinic decomposition product etc.
(Raw material latex) Conventionally well-known various natural rubber latex, such as ammonia preservation concentration natural rubber latex (about 60% of rubber part concentration) and a field latex (about 30% of rubber part concentration) extracted from the rubber tree, can be used for the latex used as the start raw material for obtaining the cationic deprotein natural rubber latex of this invention.
[0022] (Deproteinization) As mentioned above, deproteinization adds the deproteinized-natural-rubber processing agent of this invention to the above-mentioned raw material latex, and is performed by making it ripe the 1 to 3rd [about] day preferably about one week from dozens of minutes. This aging processing may be performed agitating a latex and may be performed in the condition of having put. Moreover, what is necessary is just to adjust 5-90 degrees C to 20-60 degrees C preferably, in order to perform a temperature control if needed and to make activity of an enzyme into sufficient thing. When there is a possibility that an enzyme reaction may not progress when less than 5 degrees C, and it exceeds 90 degrees C conversely, there is a possibility that an enzyme may deactivate.
[0023] Although not limited especially as purification processing of the rubber particle in a latex after the above-mentioned deproteinization, the processing which separates non-rubber components, such as a proteolysis object which condensed the latex with centrifugal separation, an ultrafiltration method, etc., and shifted underwater, and the rubber particle in a latex, and the processing which is made to condense a rubber particle with an acid etc. and is separated are mentioned, for example.
(Extent of deprotein) With the nitrogen content (N %) by the Kjeldahl method, 0.1% or less, preferably, extent of the deprotein attained by the deproteinization agent of this invention is adjusted 0.5% or less so that it may become 0.02% or less more preferably. When a nitrogen content exceeds the above-mentioned range, extent of deprotein becomes imperfection and there is a possibility that it may become impossible to fully control generating of allergy.
[0024] In addition, in this invention, as a cationic surfactant, since an alkylamine salt, alkylamine derivatives, or the 4th class ghosts of those are used, the nitrogen content for the cationic surface active agent concerned will also be contained in the nitrogen content by the Kjeldahl method. Then, in order to calculate the amount of protein in which a part for rubber is adsorbed, it is necessary to measure the amount of cationic surface active agents in the serum obtained according to centrifugal separation with total amine ** or an amelioration Epton method, to calculate the amount of the cationic surface active agent contained in a cream part, and to amend the nitrogen content of the part.
[0025] Moreover, extent of deprotein can check ** with the existence of the absorption based on the protein in an infrared absorption spectrum, and extent of absorption. Although absorption of 3320cm-1 originating in a short chain peptide or amino acid may be observed by the rubber processed by the deproteinization agent of this invention, the smaller one of absorption of 3280cm-1 originating in the giant-molecule polypeptide leading to allergy is desirable, and it is more desirable that absorption is not observed at all by 3280cm-1.
[0026] [Application of cationic deprotein natural rubber latex] It is not only possible to use for the field which uses natural rubber conventionally [, such as a glove, a contraceptive, a medical supply, length yarn, solid rubber goods, sporting goods, and a tire], but it can use suitably the cationic deproteinized natural rubber which was obtained by the manufacture approach of this invention and which removed protein highly as the adhesion and adhesives to the object charged in negative [, such as paper leaf and fiber,].
[0027]
[Example] Next, an example and the example of a comparison are given and this invention is

explained. The cationic surfactant used for the following examples and examples of a comparison is as follows.
- Lauryl amine hydrochloride () [C12H25NH2] - 70 % of the weight of HCl-- contents of an active principle, coconut amine acetate [General formula :R-NH2 -AcOH] (R=Cn Hn +1, n=8-18) : trade name by Kao Corp. "ASETAMIN 24" -- 98 % of the weight of contents, the polyoxyethylene of an active principle (10) -- cocoalkyl amine [general formula: -- R-N [(CH2 CH2 O) m H] and [(CH2 CH2 O) n H]] (m+n=10)
- Polyoxyethylene (10) stearyl amine polyoxyethylene (4 5) RARURIRU ether carboxylate [general formula :C18H37N +[(CH2 CH2 O) m O] [(CH2 CH2 O) n O] and O-OCH2 C (CH2 CH2 O)4, 5 and C12H25] (m+n=10)
- Stearyl chloride trimethylammonium () [C18H37N+] () [CH3] 3 Cl- : - Kao 28 % of the weight of trade name "Kohtamin 86W" -- contents of an active principle, and chlorination JIDESHIRU dimethylannmonium of Make [(C10H21) 2 N(CH3)+CH3 and Cl-] : The Kao Corp. make Trade name "Kohtamin D10P" -- 75 % of the weight [of contents of an active principle], and benzalkonium chloride [C14H29(CH3) 2 N(C6 H5 CH2)+, and Cl-,]: Trade name by Kao Corp. "SANIZORU C" -- 50 % of the weight [manufacture of cationic deprotein natural rubber latex] of contents of an active principle

example 1- the ion-exchange-water 167 weight section was added and diluted in the high ammonia latex 167 weight section (rubber part 100 weight section) of 60 % of the weight of part concentration for 5, 7, and 8 rubber, and it added at a rate which shows the cationic surfactant shown in a table 1, and an enzyme (a proteolytic enzyme, alkaline protease) in this table.

[0028] This latex was put at 35 degrees C for 24 hours, proteolysis processing was performed, and, subsequently at-long-intervals alignment separation was carried out by 10000rpm (gravitational acceleration 9000 [about] G) for 30 minutes. The cream part of the separated upper layer is taken out after centrifugal separation, and the ion exchange water of 15 weight sections was added, and it was made to re-distribute to the cream part 100 weight section. In this way, the obtained dispersion liquid were slushed on the glass plate, and carried out reduced pressure drying for one - two days. Then, it asked for nitrogen content with the Kjeldahl method, and considered as the index of the amount of protein which remains.

[0029] In measurement of the nitrogen content by the above-mentioned Kjeldahl method, in order to remove the effect of a cationic surfactant, the amount of surfactants in the serum after centrifugal separation was measured for the amount of surfactants in which a part for rubber is adsorbed by total amine **, and the nitrogen content was amended using this value.

After diluting the high ammonia latex of the example 6 above and adding the same deproteinization agent as an example 5 at same rate, proteolysis processing was performed like the example 5 and the part for an upper cream was taken out.

[0030] To this cream part 100 weight section, the 1-% of the weight water-solution 15 weight section of the same cationic surface active agent (stearyl chloride trimethylammonium) as having used it at the time of the above-mentioned proteolysis processing was added, it was made to re-distribute and] during 30 minutes was again performed by centrifugal separation processing [10000rpm (gravitational acceleration 9000 [about] G). Re-distribution with ion exchange water and reduced pressure drying were performed for a part for the separated cream like ejection and an example 5 after this 2nd centrifugal separation processing.

[0031] The ion-exchange-water 167 weight section was added and diluted in the high ammonia latex 167 weight section (rubber part 100 weight section) of 60 % of the weight of part concentration for one to example of comparison 5 rubber, and it added at a rate which shows the cationic surfactant shown in a table 1 in this table. Subsequently, at-long-intervals alignment separation of this latex was carried out by 10000rpm (gravitational acceleration 9000 [about] G) for 30 minutes. The cream part of the separated upper layer is taken out after centrifugal separation, and the ion exchange water of 15 weight sections was added, and it was made to re-distribute to the cream part 100 weight section.

[0032] In this way, the obtained dispersion liquid were slushed on the glass plate, and carried out reduced pressure drying for one - two days. Then, it asked for nitrogen content with the Kjeldahl method, and considered as the index of the amount of protein which remains. The class of

cationic surface active agent used in each example and the example of a comparison, an addition and the addition of a proteolytic enzyme, and the count of centrifugal separation processing are shown in a table 1.
[0033]
[A table 1]

	カチオン性界面活性剤		酵素	遠心分離
	種類	添加量*	添加量†	処理回数
実施例1	ラウリルアミン塩酸塩	7.0	0.07	1
実施例2	ココナットアミン酢酸塩	7.0	0.07	1
実施例3	ポリオキシエチレン(10)ココアルキルアミン	5.0	0.07	1
実施例4	ポリオキシエチレン(10)ステアリルアミン・ココアルキルアミン	10.0	0.07	1
実施例5	塩化ステアリルトリメチルアンモニウム	16.7	0.07	1
実施例6	塩化ステアリルトリメチルアンモニウム	16.7	0.07	2
実施例7	塩化ジデシルジメチルアンモニウム	6.7	0.07	1
実施例8	塩化ベンザルコニウム	10.0	0.07	1
比較例1	ラウリルアミン塩酸塩	7.0	—	1
比較例2	ポリオキシエチレン(10)ココアルキルアミン	5.0	—	1
比較例3	ポリオキシエチレン(10)ステアリルアミン・ココアルキルアミン	10.0	—	1
比較例4	塩化ステアリルトリメチルアンモニウム	16.7	—	1
比較例5	塩化ステアリルトリメチルアンモニウム	16.7	—	—

[0034] Among a table 1, the addition of the cationic surfactant which attached * mark shows the weight rate about the active principle of the surfactants concerned, and is the weight section to the rubber solid content 100 weight section of natural rubber latex. Moreover, the addition of the enzyme which attached ** mark is the weight section of a proteolytic enzyme (alkaline protease) to the rubber solid content 100 weight section of natural rubber latex among a table 1.
[0035] [Characterization of a latex] The following property was evaluated about the latex obtained in the above-mentioned example and the example of a comparison.
(i) According to the nitrogen content Kjeldahl method, the amount of total nitrogen in latex solid content was calculated. In addition, the value shown in tables 2 and 3 is a value which amended the nitrogen content based on the nitrogen atom in a surfactant.
[0036] (ii) About the latex which passed after initial viscosity preparation on the 1st, using BM mold viscometer, it measured on #2 or #3 rotor, rotational-speed 60rpm, and 25-degree C conditions, and this was made into initial viscosity.
(iii) The appearance of the latex in the event of passing after appearance change preparation of the latex under preservation on the 10th and the event of passing on the 30th was observed visually, and it checked whether separation with a part for a cream and serum would have arisen.

[0037] The above result is shown in a table 2.
[0038]
[A table 2]

	窒素分（重量%）	初期粘度（mPa·s）	外観変化 10日後	外観変化 30日後
実施例1	0.04	40	変化なし	変化なし
実施例2	0.04	37	変化なし	変化なし
実施例3	0.04	45	変化なし	変化なし
実施例4	0.04	45	変化なし	変化なし
実施例5	0.03	40	変化なし	変化なし
実施例6	0.02	35	変化なし	変化なし
実施例7	0.04	55	変化なし	変化なし
実施例8	0.04	90	変化なし	変化なし
比較例1	0.15	60	分離	分離
比較例2	0.13	90	分離傾向	分離
比較例3	0.13	100	分離傾向	分離傾向
比較例4	0.11	60	分離傾向	分離傾向
比較例5	0.25	30	分離	分離

[0039] By deproteinizing by the processing agent of this invention showed that the deprotein natural rubber latex by which cationicity was stabilized could be prepared so that more clearly than a table 2. On the other hand, in the example of a comparison which has not performed deproteinization by the proteolytic enzyme, the latex dissociated thoroughly, the indication to separate was seen (separation inclination), or it wrote, and the problem which stops being suitable for supply in the condition of a latex arose.

[Manufacture of cationic deprotein natural rubber latex]

The ion-exchange-water 450 weight section was added to the high ammonia latex 167 weight section (rubber part 100 weight section) of 60 % of the weight of part concentration for example 9 rubber, the alkaline protease [trade name "KP-3939" by Kao Corp.] 0.07 weight section and the stearyl chloride trimethylammonium [trade name "Kohtamin 86W" by Kao Corp.] 16.7 weight section were blended, and the total-solids concentration TSC prepared 15% of latex.

[0040] Subsequently, this latex was put at 35 degrees C for 24 hours, proteolysis processing was performed, and at-long-intervals alignment separation was carried out by 10000rpm (gravitational acceleration 9000 [about] G) for 30 minutes. The cream part of the separated upper layer is taken out after centrifugal separation, and the ion exchange water of 15 weight sections was added, and it was made to re-distribute to the cream part 100 weight section. In this way, the obtained dispersion liquid were slushed on the glass plate, and carried out reduced pressure drying for one - two days. Then, while asking for nitrogen content with the Kjeldahl method, infrared-absorption-spectrum analysis was performed.

[0041] Example 10 centrifugal-separation processing was performed twice, and also deproteinization, re-distribution for a cream, and reduced pressure drying were performed like the example 9, and measurement of nitrogen content and analysis of an infrared absorption spectrum were performed.

The ion-exchange-water 450 weight section was added to the high ammonia latex 167 weight section (rubber part 100 weight section) of 60 % of the weight of part concentration for example of comparison 6 rubber, the stearyl chloride trimethylammonium [trade name "Kohtamin 86W" by Kao Corp.] 16.7 weight section was blended, and the total-solids concentration TSC prepared 15% of latex.

[0042] Subsequently, this latex was put at 35 degrees C for 24 hours, proteolysis processing was performed, and at-long-intervals alignment separation was carried out by 10000rpm (gravitational acceleration 9000 [about] G) for 30 minutes. The cream part of the separated upper layer is taken out after centrifugal separation, and the ion exchange water of 15 weight sections was added, and it was made to re-distribute to the cream part 100 weight section. In this way, the obtained dispersion liquid were slushed on the glass plate, and carried out reduced pressure drying for one - two days. Then, while asking for nitrogen content with the Kjeldahl method,

infrared-absorption-spectrum analysis was performed.
[0043] (Measurement of an infrared absorption spectrum) The solid film used on the occasion of measurement of the nitrogen content in examples 9 and 10 and the example 6 of a comparison was carried on the KBr disk, and the infrared absorption spectrum was measured. The result of the nitrogen content of examples 9 and 10 and the example 6 of a comparison and an infrared absorption spectrum is shown in a table 3. Moreover, infrared-absorption-spectrum drawing is shown in drawing 1 -3.
[0044]
[A table 3]

	窒素含有量	赤外吸収スペクトル	
	N (%)	3320 cm^{-1}	3280 cm^{-1}
実施例9	0.038	検出	僅かに検出
実施例10	0.018	検出	不検出
比較例6	0.11	不検出	検出

[0045] In the example 10, although absorption of 3320cm-1 originating in a short chain peptide or amino acid was detected, the nitrogen content was very low and absorption originating in a giant-molecule polypeptide was not detected at all, so that more clearly than a table 3. Therefore, generating of allergy was able to obtain the safe latex to the fully controlled body. In the example 9, although absorption of 3280cm-1 originating in a giant-molecule polypeptide was detected slightly, since the nitrogen content was controlled to the very low value like the example 10, it was suggested that the safe latex was obtained to the body with which generating of allergy was fully controlled.
[0046] On the other hand, in the example 6 of a comparison, it did not come out as the nitrogen content was large, and since absorption of 3280cm-1 originating in a giant-molecule polypeptide was detected, it was suggested that there is a possibility of generating allergy. Since at least one sort of surfactants chosen from the group which consists of a proteolytic enzyme, alkylamine salts and alkylamine derivatives, and the 4th class ghosts of those into the processing agent concerned are contained as an active principle according to the deproteinization agent of this invention as explained in full detail above, the protein in natural rubber can be removed efficiently and stable cationic deprotein natural rubber latex can be prepared by the simple approach.

[Translation done.]

* NOTICES *

TECHNICAL FIELD

[Field of the Invention] This invention relates to the manufacture approach of the deproteinization agent for obtaining the deprotein [in which it is stable and cationicity is shown] natural rubber latex from which the protein in natural rubber was removed, and the cationic deprotein natural rubber latex using it.

[Translation done.]

PRIOR ART

[Description of the Prior Art] Generally, although natural rubber latex contains protein as non-rubber components other than a rubber component, since the class and amount of this protein change with places of production, production stages, etc. of a latex, last quality, a last vulcanization property, etc. of a natural rubber product are made to produce dispersion, or electrical properties, such as mechanical characteristics, such as a creep property and aging resistance, and insulation, etc. have become the cause of reducing the quality of a natural rubber product itself.

[0003] When a natural rubber product is furthermore used in recent years, the protein in natural rubber becomes a cause and the case where the allergy symptom of a strong I-beam is caused is reported. Although washing concentration of the natural rubber latex was carried out with water or the approach of adding a surfactant and carrying out washing concentration was indicated to these problems, these approaches of extent of deprotein were insufficient. To these problems, to aim at solution by the approach of removing protein to altitude is tried from the natural rubber latex of the disclosure to JP,6-56904,A, JP,6-56905,A, and JP,6-56906,A. After this approach adds a proteolytic enzyme (protease) and the surfactant of anionic or the Nonion nature to natural rubber latex and disassembles protein, by purification processing by centrifugal separation etc., it separates a cream-like rubber component and removes protein.

[0004] However, the surfactant used by the above-mentioned approach is the thing of anionic or the Nonion nature, and is in the condition of the rubber particle in deprotein natural rubber latex also being charged in negative, or not having a polarity. Therefore, it was unsuitable to have used this latex for raw materials, such as the object-ed charged in negative from the first, for example, fiber, and an adhesive to a paper product.

[Translation done.]

EFFECT OF THE INVENTION

[The means for solving a technical problem and an effect of the invention] this invention persons came to complete a header and this invention for the completely new data that generating of an allergic response was fully controlled and that a latex with the high safety to the body can also be obtained while being able to get the stable latex which fully controlled generating of a congelation, when deproteinizing by blending a specific cationic surfactant with natural rubber latex, as a result of repeating research wholeheartedly, in order to solve the above-mentioned technical problem.
[0009] That is, the deproteinization agent of this invention is characterized by consisting of a proteolytic enzyme and one or more sorts of cationic surfactants chosen from the group which consists of an alkylamine salt, alkylamine derivatives, and the 4th class ghosts of those. In case the distributed condition of the rubber particle destabilized with deprotein is stabilized with a surfactant like conventional deprotein natural rubber latex according to the deproteinization agent of above-mentioned this invention, a latex is not electrified in negative. Moreover, since the latex to which deproteinization was performed is made to contain a specific cationic surface active agent, generating of a congelation can fully be controlled and a stable latex can be offered. Furthermore, since the protein in natural rubber latex is removed by deproteinization, generating of an allergic response can fully be controlled and natural rubber latex with the high safety to the body can be offered.
[0010] The manufacture approach of the cationic deprotein natural rubber latex of this invention is characterized by adding the deproteinization agent of above-mentioned this invention to a field latex or an ammoniation latex, and refining the rubber particle in a latex. In the manufacture approach of the above-mentioned cationic deprotein natural rubber latex, as for the addition of a deproteinization agent, it is desirable to add so that the content of a surfactant may serve as 0.1 - 20 weight section to the rubber solid content 100 weight section in a latex, and it is desirable to add so that the content of a proteolytic enzyme may serve as 0.0001 - 20 weight section to the rubber solid content 100 weight section in a latex.
[0011]
[Embodiment of the Invention] Hereafter, this invention is explained to a detail.
[Deproteinization agent]
(Proteolytic enzyme) Although a well-known thing is especially usable and is not conventionally limited as a proteolytic enzyme used for the deproteinization agent of this invention, alkaline protease etc. is suitable, for example. As the origin of a protease, although you may be which things, such as a thing of the bacteria origin, a thing of the mold origin, and a thing of the yeast origin, in these, it is the thing of the bacteria origin and especially the thing of a Bacillus group is desirable. Moreover, it is also possible to use together enzymes, such as lipase, esterase, an amylase, a laccase, and a cellulase.
[0012] The protease KAP by Kao Corp. in which especially the proteolytic enzyme used for this invention has the resistance over a surfactant also in the above is used suitably. When using alkaline protease as a proteolytic enzyme, it is preferably suitable for the activity [the measured value by the method of improving the Anson-haemoglobin complex method (22 Anson.M.L., J.Gen.Physiol., 79 (1938))] that it is the range of 1 - 25 APU/g 0.1 to 50 APU/g.

[0013] In case the deproteinization agent of this invention is used for the amount of the above-mentioned proteolytic enzyme used, it is desirable to add so that it may become 0.0001 - 20 weight section to the rubber part 100 weight section in natural rubber latex, and it is more desirable to add in the range of 0.001 - 10 weight section. The effectiveness of fully being able to disassemble the protein in a latex as the amount of the proteolytic enzyme used is said within the limits, and the activity of an enzyme being held, or balancing the amount of the enzyme used can be discovered effectively, and it becomes advantageous in cost.
[0014] (Surface active agent) It faces manufacturing the cationic deprotein natural rubber latex of this invention, (i) The distributed stability and preservation stability of the (ii) latex should be further excelled in the latex for the purpose of distributing a part for rubber in the stable condition at the time of decomposition processing of protein, and the rubber particle in a latex is just electrified, and one or more sorts of cationic surfactants as a stabilizer are used into a latex for the purpose of considering as the underwater suspension of a cation charged particle.
[0015] As a cationic surfactant used for this invention, an alkylamine salt, alkylamine derivatives, and the 4th class ghosts of those are mentioned. Although the salt of primary amine, secondary amine, and tertiary amine is mentioned and it is not especially limited as the above-mentioned alkylamine salt, as a salt, a hydrochloride, phosphate, acetate, alkyl-sulfuric-acid ester, alkylbenzene sulfonic acid, an alkyl naphthalene sulfonic acid, a fatty acid, an organic acid, alkyl phosphoric ester, an alkyl ether carboxylic acid, an alkylamide ether carboxylic acid, anionic oligomer, an anionic polymer, etc. are mentioned, for example.
[0016] The above-mentioned alkylamine derivative has at least one of an ester group, a ether group, and amide groups in intramolecular. It is. For example, polyoxyalkylene (AO) alkylamine and its salt, An alkyl ester amine (AO addition product is included) and its salt, an alkyl ether amine (AO addition product is included), and its salt, An alkylamide amine (AO addition product is included) and its salt, an alkyl ester amide amine (AO addition product is included), and its salt, An alkyl ether amide amine (AO addition product is included), its salt, etc. are mentioned. As a salt For example, a hydrochloride, phosphate, acetate, alkyl-sulfuric-acid ester, alkylbenzene sulfonic acid, An alkyl naphthalene sulfonic acid, a fatty acid, an organic acid, alkyl phosphoric ester, an alkyl ether carboxylic acid, an alkylamide ether carboxylic acid, anionic oligomer, an anionic polymer, etc. are mentioned.
[0017] As an example of the above-mentioned acetate, coconut amine acetate, stearyl amine acetate, etc. are mentioned, for example. Although the above-mentioned alkylamine salt and especially the alkyl group in an alkylamine derivative are not limited, the thing of the shape of the shape of a straight chain, branched-chain, or Guerbet of carbon numbers 8-22 is usually mentioned. as the 4th class ghost of the above-mentioned alkylamine salt and an alkylamine derivative -- the above-mentioned alkylamine salt and an alkylamine derivative -- for example, methyl chloride, a methyl bromide, a dimethyl sulfate, a diethyl sulfate, etc. -- the -- what was formed into 4 class is mentioned.
[0018] As said quarternary ammonium salt, what has the alkyl group of carbon numbers 8-22, for example is mentioned, and dialkyl dimethylannmonium halide; trialkyl methylammonium halide; dialkyl benzyl methylammonium halide; alkyl benzyl dimethylannmonium halide, such as alkyl trimethylammonium halide; distearyldimethylbenzylammonium halide, such as lauryl trimethylammonium halide, cetyl trimethylammonium halide, and stearyl trimethyl ammonium halide, etc. is mentioned in more detail.
[0019] Also in the cationic surface active agent of the above-mentioned instantiation, since the stabilization effect of a latex is excellent, cetyl trimethylammonium chloride (CTAC) and especially stearyl trimethylammonium chloride are used suitable for this invention. In case the deproteinization agent of this invention is used for the amount of the above-mentioned cationic surfactant used, it is desirable to add so that it may become 0.1 - 20 weight section to the rubber solid content 100 weight section in natural rubber latex, and it is more desirable to add in the range of 0.5 - 15 weight section. The hygroscopicity of solid rubber when adsorption of the cationic surface active agent to the rubber particle in a latex dries a next door and a latex enough as the amount of the cationic surface active agent used is said within the limits is maintained low, can discover effectively the effectiveness of balancing the amount used, and

becomes advantageous in cost.
[0020] (Other additives) Other additives, such as pH regulator, may be used together on the occasion of using the above-mentioned proteolytic enzyme and a cationic surfactant as a deproteinization agent. As the above-mentioned pH regulator, acetate; sulfates, such as phosphate; potassium acetate, such as a potassium dihydrogenphosphate, potassium phosphate, and disodium hydrogenphosphate, and sodium acetate, a hydrochloride, a nitrate, citrate, succinate, ammonia, a sodium hydroxide, a potassium hydroxide, a sodium carbonate, a sodium hydrogencarbonate, etc. are mentioned, for example.
[0021] The [manufacture approach of cationic deprotein natural rubber latex] It is suitable to deproteinize by adding the deproteinized-natural-rubber processing agent of this invention to the natural rubber latex which serves as a start raw material in manufacture in the cationic deprotein natural rubber latex using the deproteinized-natural-rubber processing agent of this invention, to perform purification processing of a latex particle subsequently, and to use the approach of removing a proteinic decomposition product etc.
(Raw material latex) Conventionally well-known various natural rubber latex, such as ammonia preservation concentration natural rubber latex (about 60% of rubber part concentration) and a field latex (about 30% of rubber part concentration) extracted from the rubber tree, can be used for the latex used as the start raw material for obtaining the cationic deprotein natural rubber latex of this invention.
[0022] (Deproteinization) As mentioned above, deproteinization adds the deproteinized-natural-rubber processing agent of this invention to the above-mentioned raw material latex, and is performed by making it ripe the 1 to 3rd [about] day preferably about one week from dozens of minutes. This aging processing may be performed agitating a latex and may be performed in the condition of having put. Moreover, what is necessary is just to adjust 5-90 degrees C to 20-60 degrees C preferably, in order to perform a temperature control if needed and to make activity of an enzyme into sufficient thing. When there is a possibility that an enzyme reaction may not progress when less than 5 degrees C, and it exceeds 90 degrees C conversely, there is a possibility that an enzyme may deactivate.
[0023] Although not limited especially as purification processing of the rubber particle in a latex after the above-mentioned deproteinization, the processing which separates non-rubber components, such as a proteolysis object which condensed the latex with centrifugal separation, an ultrafiltration method, etc., and shifted underwater, and the rubber particle in a latex, and the processing which is made to condense a rubber particle with an acid etc. and is separated are mentioned, for example.
(Extent of deprotein) With the nitrogen content (N %) by the Kjeldahl method, 0.1% or less, preferably, extent of the deprotein attained by the deproteinization agent of this invention is adjusted 0.5% or less so that it may become 0.02% or less more preferably. When a nitrogen content exceeds the above-mentioned range, extent of deprotein becomes imperfection and there is a possibility that it may become impossible to fully control generating of allergy.
[0024] In addition, in this invention, as a cationic surfactant, since an alkylamine salt, alkylamine derivatives, or the 4th class ghosts of those are used, the nitrogen content for the cationic surface active agent concerned will also be contained in the nitrogen content by the Kjeldahl method. Then, in order to calculate the amount of protein in which a part for rubber is adsorbed, it is necessary to measure the amount of cationic surface active agents in the serum obtained according to centrifugal separation with total amine ** or an amelioration Epton method, to calculate the amount of the cationic surface active agent contained in a cream part, and to amend the nitrogen content of the part.
[0025] Moreover, extent of deprotein can check ** with the existence of the absorption based on the protein in an infrared absorption spectrum, and extent of absorption. Although absorption of 3320cm-1 originating in a short chain peptide or amino acid may be observed by the rubber processed by the deproteinization agent of this invention, the smaller one of absorption of 3280cm-1 originating in the giant-molecule polypeptide leading to allergy is desirable, and it is more desirable that absorption is not observed at all by 3280cm-1.
[0026] [Application of cationic deprotein natural rubber latex] It is not only possible to use for

the field which uses natural rubber conventionally [, such as a glove, a contraceptive, a medical supply, length yarn, solid rubber goods, sporting goods, and a tire], but it can use suitably the cationic deproteinized natural rubber which was obtained by the manufacture approach of this invention and which removed protein highly as the adhesion and adhesives to the object charged in negative [, such as paper leaf and fiber,].

[Translation done.]

* NOTICES *

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The cationic natural rubber latex which, on the other hand, blended with the 94-95th page of "Natural Rubber Science and Technology" (A.D.Roberts editing, the Oxford university publication, 1988 annual publications) the cetyl trimethylammonium bromide (CTAB) which is a cationic surface active agent is indicated. Although the latex which consists of a rubber particle which has a cation will be obtained like this reference if the cationic surfactant of sufficient amount for natural rubber latex is added, when processed underwater, the adhesion force with fiber, paper leaf, etc. which are charged in negative can be raised by making a latex into cationicity in this way.

[0006] However, only by adding a cationic surfactant, deprotein cannot be attained with a natural thing and safe natural rubber latex cannot be offered to the body -- an allergic response arises. Furthermore, when a cationic surfactant is only added, the problem that a stable latex -- viscosity rises with time and a congelation is generated -- cannot be obtained is in natural rubber latex.

[0007] Then, the object of this invention shows cationicity, and its safety is high, and it is offering the deproteinization agent for obtaining stable natural rubber latex, and the manufacture approach of the cationic deprotein natural rubber latex using it.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

EXAMPLE

[Example] Next, an example and the example of a comparison are given and this invention is explained. The cationic surfactant used for the following examples and examples of a comparison is as follows.
- Lauryl amine hydrochloride () [C12H25NH2] - 70 % of the weight of HCl-- contents of an active principle, coconut amine acetate [General formula :R-NH2 -AcOH] (R=Cn Hn +1, n=8-18) : trade name by Kao Corp. "ASETAMIN 24" -- 98 % of the weight of contents, the polyoxyethylene of an active principle (10) -- cocoalkyl amine [general formula: -- R-N [(CH2 CH2 O) m H] and [(CH2 CH2 O) n H]] (m+n=10)
- Polyoxyethylene (10) stearyl amine polyoxyethylene (4 5) RARURIRU ether carboxylate [general formula :C18H37N +[(CH2 CH2 O) m O] [(CH2 CH2 O) n O] and O-OCH2 C (CH2 CH2 O)4, 5 and C12H25] (m+n=10)
- Stearyl chloride trimethylammonium () [C18H37N+] () [CH3] 3 Cl- : - Kao 28 % of the weight of trade name "Kohtamin 86W" -- contents of an active principle, and chlorination JIDESHIRU dimethylannmonium of Make [(C10H21) 2 N(CH3)+CH3 and Cl-] : The Kao Corp. make Trade name "Kohtamin D10P" -- 75 % of the weight [of contents of an active principle], and benzalkonium chloride [C14H29(CH3) 2 N(C6 H5 CH2)+, and Cl-,]: Trade name by Kao Corp. "SANIZORU C" -- 50 % of the weight [manufacture of cationic deprotein natural rubber latex] of contents of an active principle
example 1- the ion-exchange-water 167 weight section was added and diluted in the high ammonia latex 167 weight section (rubber part 100 weight section) of 60 % of the weight of part concentration for 5, 7, and 8 rubber, and it added at a rate which shows the cationic surfactant shown in a table 1, and an enzyme (a proteolytic enzyme, alkaline protease) in this table.
[0028] This latex was put at 35 degrees C for 24 hours, proteolysis processing was performed, and, subsequently at-long-intervals alignment separation was carried out by 10000rpm (gravitational acceleration 9000 [about] G) for 30 minutes. The cream part of the separated upper layer is taken out after centrifugal separation, and the ion exchange water of 15 weight sections was added, and it was made to re-distribute to the cream part 100 weight section. In this way, the obtained dispersion liquid were slushed on the glass plate, and carried out reduced pressure drying for one - two days. Then, it asked for nitrogen content with the Kjeldahl method, and considered as the index of the amount of protein which remains.
[0029] In measurement of the nitrogen content by the above-mentioned Kjeldahl method, in order to remove the effect of a cationic surfactant, the amount of surfactants in the serum after centrifugal separation was measured for the amount of surfactants in which a part for rubber is adsorbed by total amine **, and the nitrogen content was amended using this value.
After diluting the high ammonia latex of the example 6 above and adding the same deproteinization agent as an example 5 at same rate, proteolysis processing was performed like the example 5 and the part for an upper cream was taken out.
[0030] To this cream part 100 weight section, the 1-% of the weight water-solution 15 weight section of the same cationic surface active agent (stearyl chloride trimethylammonium) as having used it at the time of the above-mentioned proteolysis processing was added, it was made to re-distribute and] during 30 minutes was again performed by centrifugal separation processing

[10000rpm (gravitational acceleration 9000 [about] G). Re-distribution with ion exchange water and reduced pressure drying were performed for a part for the separated cream like ejection and an example 5 after this 2nd centrifugal separation processing.
[0031] The ion-exchange-water 167 weight section was added and diluted in the high ammonia latex 167 weight section (rubber part 100 weight section) of 60 % of the weight of part concentration for one to example of comparison 5 rubber, and it added at a rate which shows the cationic surfactant shown in a table 1 in this table. Subsequently, at-long-intervals alignment separation of this latex was carried out by 10000rpm (gravitational acceleration 9000 [about] G) for 30 minutes. The cream part of the separated upper layer is taken out after centrifugal separation, and the ion exchange water of 15 weight sections was added, and it was made to re-distribute to the cream part 100 weight section.
[0032] In this way, the obtained dispersion liquid were slushed on the glass plate, and carried out reduced pressure drying for one - two days. Then, it asked for nitrogen content with the Kjeldahl method, and considered as the index of the amount of protein which remains. The class of cationic surface active agent used in each example and the example of a comparison, an addition and the addition of a proteolytic enzyme, and the count of centrifugal separation processing are shown in a table 1.
[0033]
[A table 1]

	カチオン性界面活性剤		酵 素	遠心分離
	種　　類	添加量*	添加量†	処理回数
実施例 1	ラウリルアミン塩酸塩	7.0	0.07	1
実施例 2	ココナットアミン酢酸塩	7.0	0.07	1
実施例 3	ポリオキシエチレン(10)ココアルキルアミン	5.0	0.07	1
実施例 4	ポリオキシエチレン(10)ステアリルアミン・ココアルキルアミン	10.0	0.07	1
実施例 5	塩化ステアリルトリメチルアンモニウム	16.7	0.07	1
実施例 6	塩化ステアリルトリメチルアンモニウム	16.7	0.07	2
実施例 7	塩化ジデシルジメチルアンモニウム	6.7	0.07	1
実施例 8	塩化ベンザルコニウム	10.0	0.07	1
比較例 1	ラウリルアミン塩酸塩	7.0	—	1
比較例 2	ポリオキシエチレン(10)ココアルキルアミン	5.0	—	1
比較例 3	ポリオキシエチレン(10)ステアリルアミン・ココアルキルアミン	10.0	—	1
比較例 4	塩化ステアリルトリメチルアンモニウム	16.7	—	1
比較例 5	塩化ステアリルトリメチルアンモニウム	16.7	—	—

[0034] Among a table 1, the addition of the cationic surfactant which attached * mark shows the weight rate about the active principle of the surfactants concerned, and is the weight section to the rubber solid content 100 weight section of natural rubber latex. Moreover, the addition of the enzyme which attached ** mark is the weight section of a proteolytic enzyme (alkaline protease) to the rubber solid content 100 weight section of natural rubber latex among a table 1.
[0035] [Characterization of a latex] The following property was evaluated about the latex obtained in the above-mentioned example and the example of a comparison.
(i) According to the nitrogen content Kjeldahl method, the amount of total nitrogen in latex solid content was calculated. In addition, the value shown in tables 2 and 3 is a value which amended the nitrogen content based on the nitrogen atom in a surfactant.
[0036] (ii) About the latex which passed after initial viscosity preparation on the 1st, using BM mold viscometer, it measured on #2 or #3 rotor, rotational-speed 60rpm, and 25-degree C conditions, and this was made into initial viscosity.
(iii) The appearance of the latex in the event of passing after appearance change preparation of the latex under preservation on the 10th and the event of passing on the 30th was observed

visually, and it checked whether separation with a part for a cream and serum would have arisen.

[0037] The above result is shown in a table 2.
[0038]
[A table 2]

	窒素分 (重量%)	初期粘度 (mPa·s)	外観変化	
			10日後	30日後
実施例1	0.04	40	変化なし	変化なし
実施例2	0.04	37	変化なし	変化なし
実施例3	0.04	45	変化なし	変化なし
実施例4	0.04	45	変化なし	変化なし
実施例5	0.03	40	変化なし	変化なし
実施例6	0.02	35	変化なし	変化なし
実施例7	0.04	55	変化なし	変化なし
実施例8	0.04	90	変化なし	変化なし
比較例1	0.15	60	分離	分離
比較例2	0.13	90	分離傾向	分離
比較例3	0.13	100	分離傾向	分離傾向
比較例4	0.11	60	分離傾向	分離傾向
比較例5	0.25	30	分離	分離

[0039] By deproteinizing by the processing agent of this invention showed that the deprotein natural rubber latex by which cationicity was stabilized could be prepared so that more clearly than a table 2. On the other hand, in the example of a comparison which has not performed deproteinization by the proteolytic enzyme, the latex dissociated thoroughly, the indication to separate was seen (separation inclination), or it wrote, and the problem which stops being suitable for supply in the condition of a latex arose.
[Manufacture of cationic deprotein natural rubber latex]
The ion-exchange-water 450 weight section was added to the high ammonia latex 167 weight section (rubber part 100 weight section) of 60 % of the weight of part concentration for example 9 rubber, the alkaline protease [trade name "KP-3939" by Kao Corp.] 0.07 weight section and the stearyl chloride trimethylammonium [trade name "Kohtamin 86W" by Kao Corp.] 16.7 weight section were blended, and the total-solids concentration TSC prepared 15% of latex.
[0040] Subsequently, this latex was put at 35 degrees C for 24 hours, proteolysis processing was performed, and at-long-intervals alignment separation was carried out by 10000rpm (gravitational acceleration 9000 [about] G) for 30 minutes. The cream part of the separated upper layer is taken out after centrifugal separation, and the ion exchange water of 15 weight sections was added, and it was made to re-distribute to the cream part 100 weight section. In this way, the obtained dispersion liquid were slushed on the glass plate, and carried out reduced pressure drying for one - two days. Then, while asking for nitrogen content with the Kjeldahl method, infrared-absorption-spectrum analysis was performed.
[0041] Example 10 centrifugal-separation processing was performed twice, and also deproteinization, re-distribution for a cream, and reduced pressure drying were performed like the example 9, and measurement of nitrogen content and analysis of an infrared absorption spectrum were performed.
The ion-exchange-water 450 weight section was added to the high ammonia latex 167 weight section (rubber part 100 weight section) of 60 % of the weight of part concentration for example of comparison 6 rubber, the stearyl chloride trimethylammonium [trade name "Kohtamin 86W" by Kao Corp.] 16.7 weight section was blended, and the total-solids concentration TSC prepared 15% of latex.
[0042] Subsequently, this latex was put at 35 degrees C for 24 hours, proteolysis processing was performed, and at-long-intervals alignment separation was carried out by 10000rpm (gravitational

acceleration 9000 [about] G) for 30 minutes. The cream part of the separated upper layer is taken out after centrifugal separation, and the ion exchange water of 15 weight sections was added, and it was made to re-distribute to the cream part 100 weight section. In this way, the obtained dispersion liquid were slushed on the glass plate, and carried out reduced pressure drying for one - two days. Then, while asking for nitrogen content with the Kjeldahl method, infrared-absorption-spectrum analysis was performed.

[0043] (Measurement of an infrared absorption spectrum) The solid film used on the occasion of measurement of the nitrogen content in examples 9 and 10 and the example 6 of a comparison was carried on the KBr disk, and the infrared absorption spectrum was measured. The result of the nitrogen content of examples 9 and 10 and the example 6 of a comparison and an infrared absorption spectrum is shown in a table 3. Moreover, infrared-absorption-spectrum drawing is shown in drawing 1 -3.

[0044]

[A table 3]

	窒素含有量 N (%)	赤外吸収スペクトル 3320 cm^{-1}	赤外吸収スペクトル 3280 cm^{-1}
実施例 9	0.038	検出	僅かに検出
実施例 10	0.018	検出	不検出
比較例 6	0.11	不検出	検出

[0045] In the example 10, although absorption of 3320cm-1 originating in a short chain peptide or amino acid was detected, the nitrogen content was very low and absorption originating in a giant-molecule polypeptide was not detected at all, so that more clearly than a table 3. Therefore, generating of allergy was able to obtain the safe latex to the fully controlled body. In the example 9, although absorption of 3280cm-1 originating in a giant-molecule polypeptide was detected slightly, since the nitrogen content was controlled to the very low value like the example 10, it was suggested that the safe latex was obtained to the body with which generating of allergy was fully controlled.

[0046] On the other hand, in the example 6 of a comparison, it did not come out as the nitrogen content was large, and since absorption of 3280cm-1 originating in a giant-molecule polypeptide was detected, it was suggested that there is a possibility of generating allergy. Since at least one sort of surfactants chosen from the group which consists of a proteolytic enzyme, alkylamine salts and alkylamine derivatives, and the 4th class ghosts of those into the processing agent concerned are contained as an active principle according to the deproteinization agent of this invention as explained in full detail above, the protein in natural rubber can be removed efficiently and stable cationic deprotein natural rubber latex can be prepared by the simple approach.

[Translation done.]

* NOTICES *

DESCRIPTION OF DRAWINGS

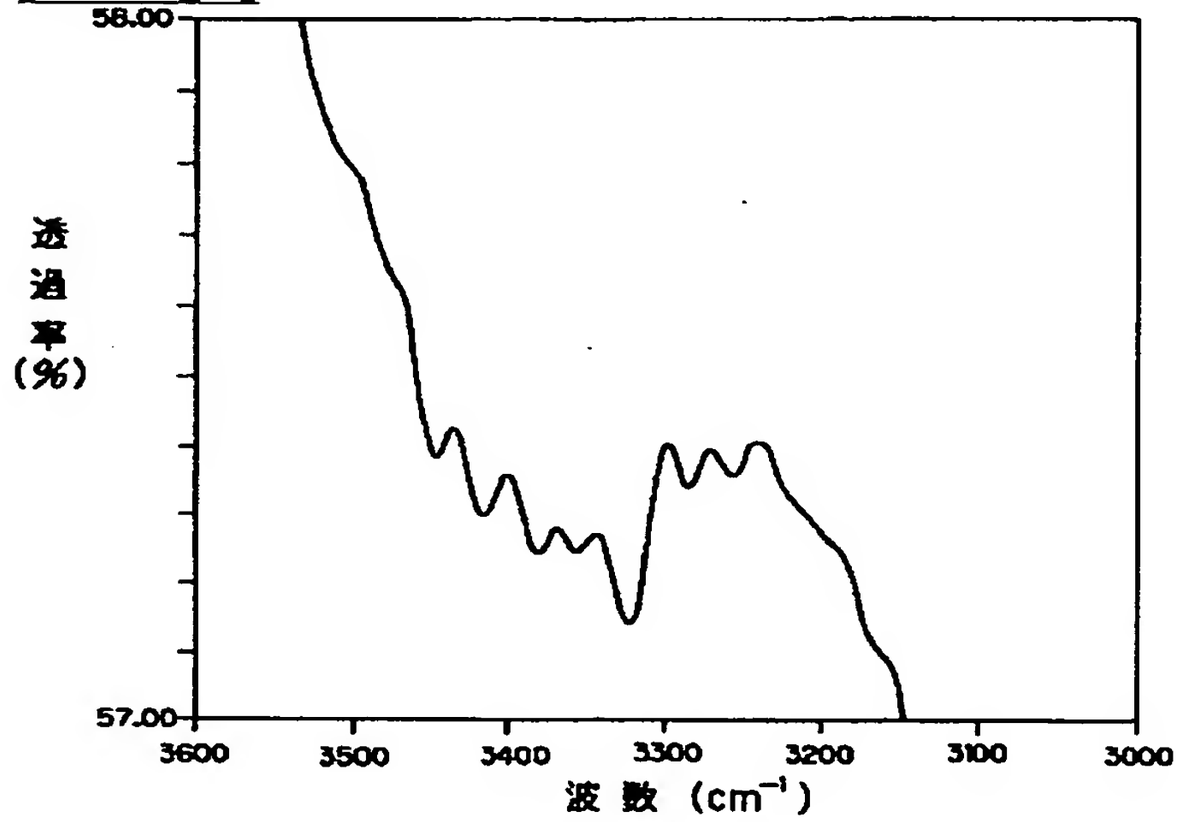
[Brief Description of the Drawings]
[Drawing 1] It is infrared-absorption-spectrum drawing of the solid film obtained in the example 9.
[Drawing 2] It is infrared-absorption-spectrum drawing of the solid film obtained in the example 10.
[Drawing 3] It is infrared-absorption-spectrum drawing of the solid film obtained in the example 6 of a comparison.

[Translation done.]

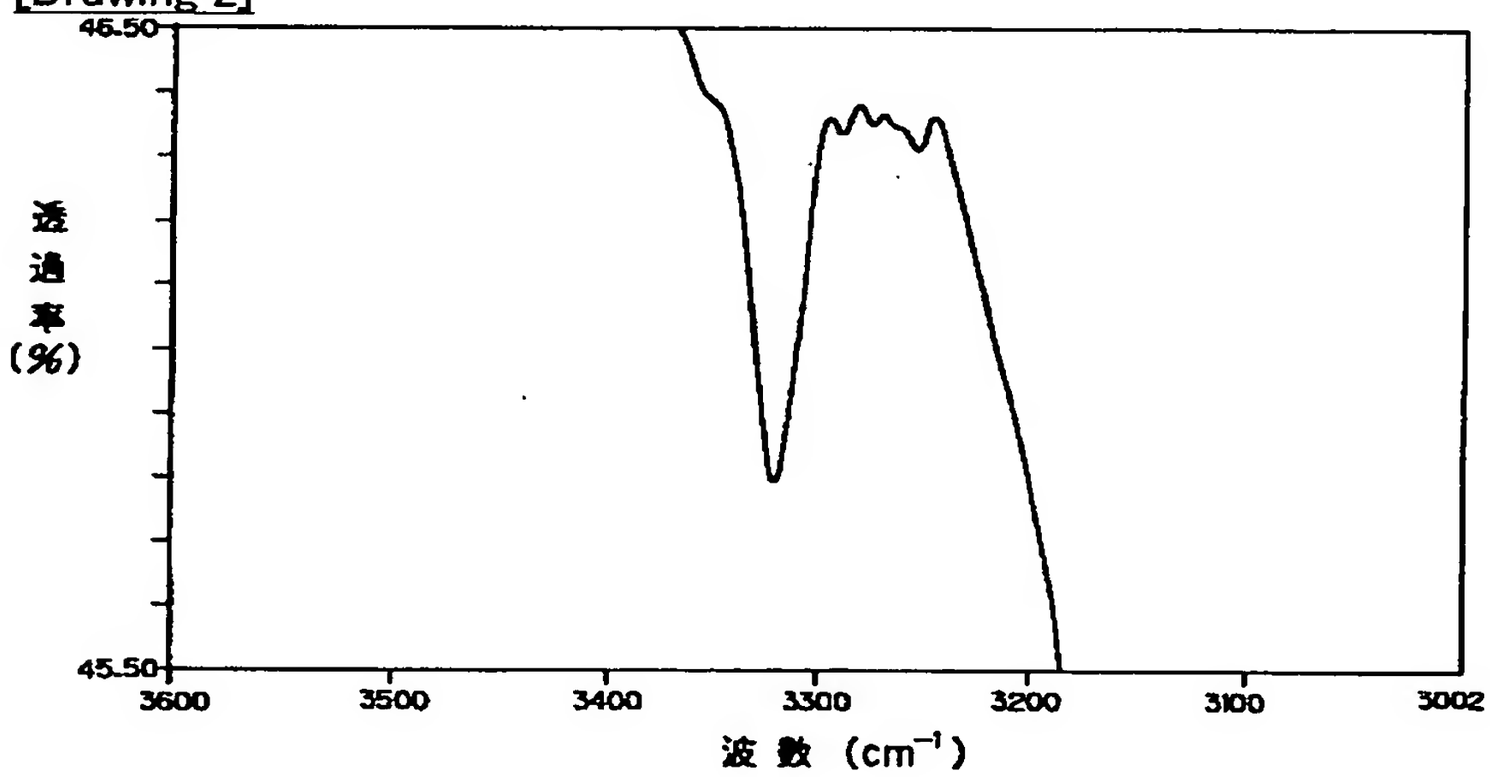
* NOTICES *

DRAWINGS

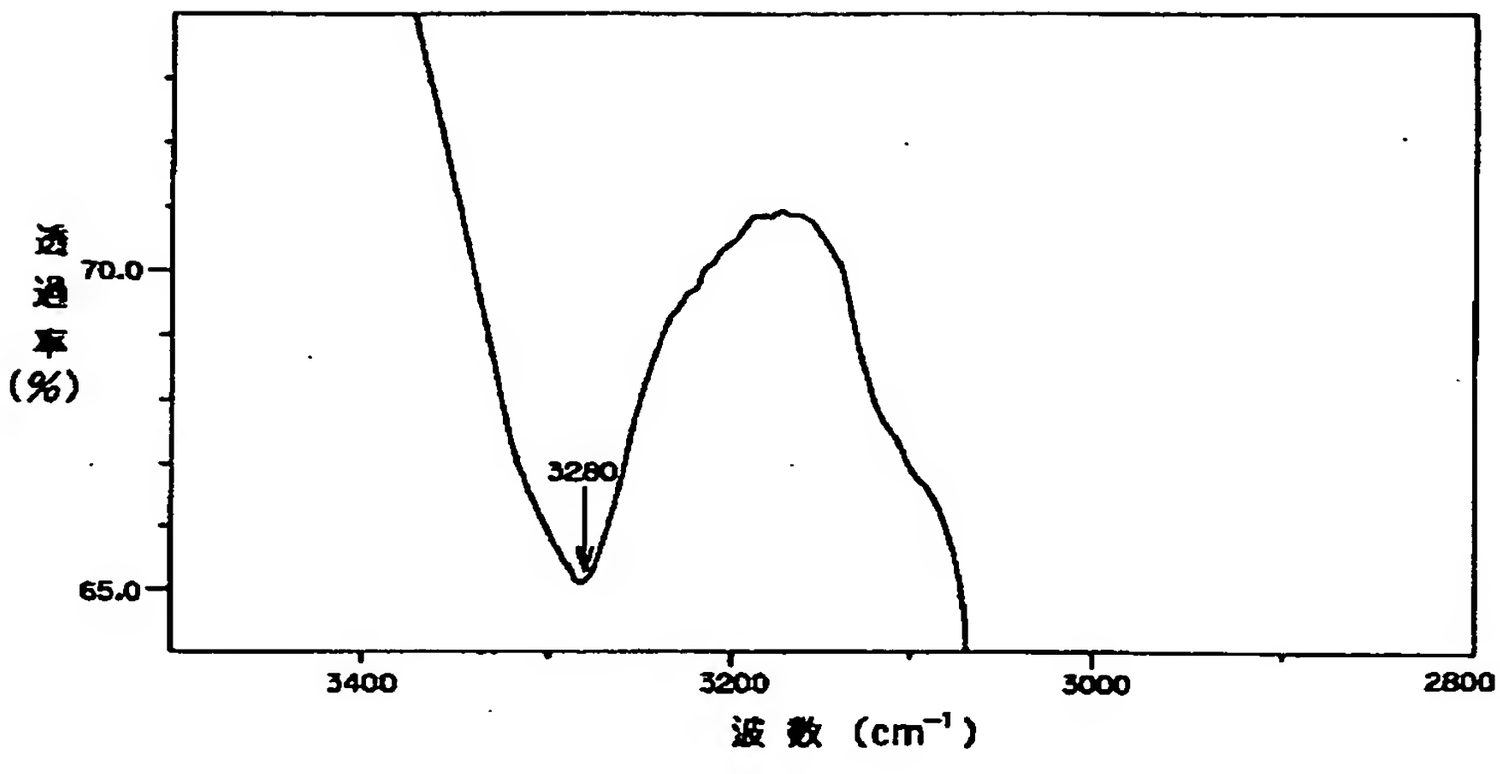
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]